

Fuel Effects on Emissions Control Technologies

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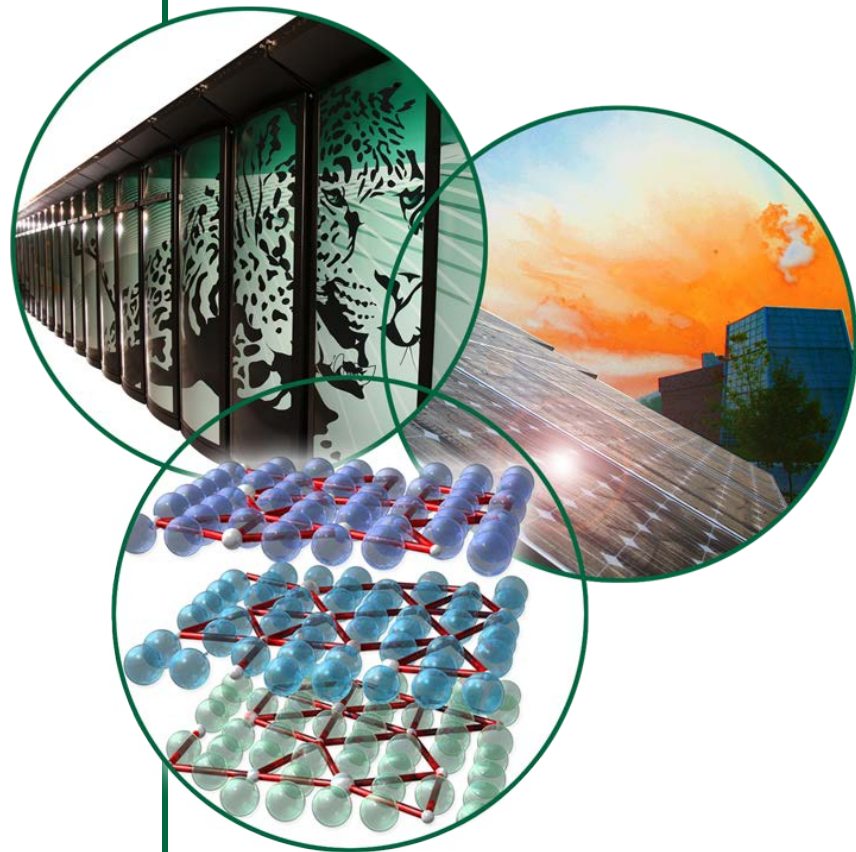
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Project Overview

Timeline

- Project is ongoing but re-focused each year to address current DOE and industry needs.
 - FY12 start: Fuel & Lubes GDI PM
 - FY10 start: Lean-Ethanol LNC
 - FY09 start: Biodiesel-based Na
 - FY08 start: EGR cooler fouling

Budget

- Funding received in
 - FY12: \$1.445M
 - FY13: \$750K (expected; includes \$200K from Lubes Program)

Barriers

- Inadequate data and predictive tools for fuel effects on emissions and emission control system impacts. (2.4 D)
- Inadequate data on long-term impact of fuel and lubricants on engines and emissions control systems. (2.4 E)

Partners

- Collaborators and their roles
 - CLEERS: Evaluation protocols
 - Cummins/Ford/GM/Modine: technical guidance
 - NREL/Ford/MECA/NBB: Biodiesel-aged emissions control devices
 - Research Personnel
 - University of Tennessee
 - University of Michigan
 - Chalmers University

Objectives and Relevance



Objective: Provide data in support of predictive tools that can be used to understand fuel-property impacts on combustion and emissions control systems.

Relevance: Addresses Fuels Technology barriers D and E: Inadequate data and predictive tools for fuel effects on emissions and emission control system impacts and inadequate data on long-term impacts of fuel and lubricants on engines and emission control systems.

Changes in fuel properties, whether caused by emerging fuel sources, increasing blend levels, or broadened market availability can:

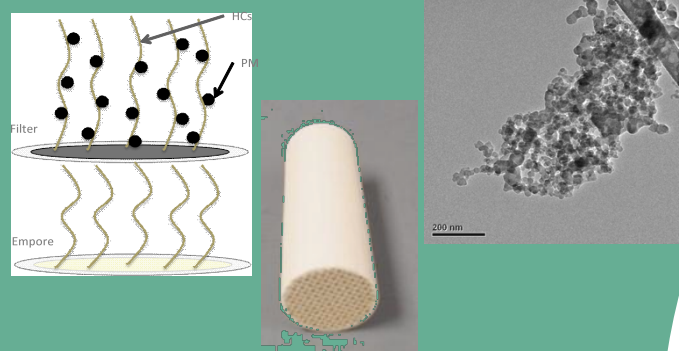
- cause unintended and undesirable issues
- offer new opportunities for component and system-level fuel efficiency benefits

Milestones

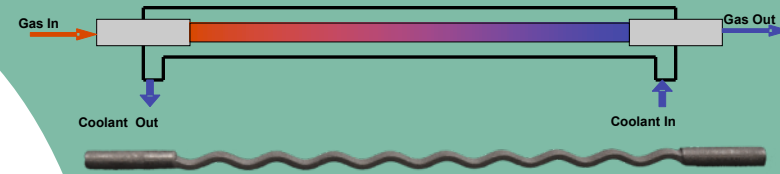
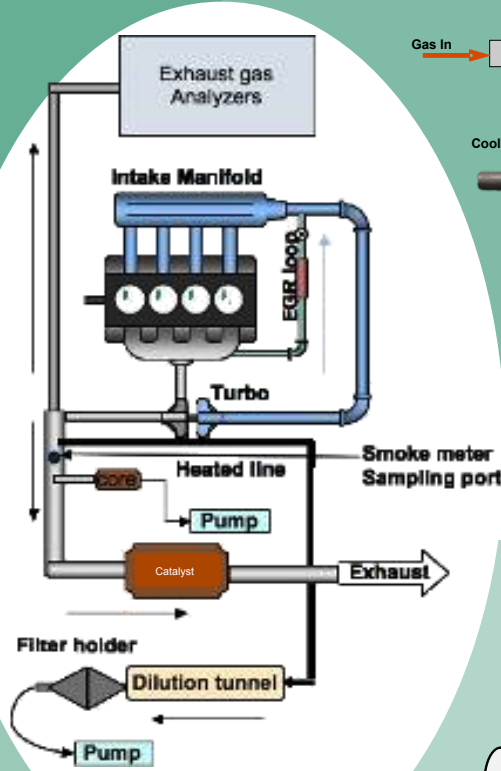
- **Fuel Formulation Impacts on EGR System Performance**
 - Characterize conditions that cause effectiveness stabilization and plugging.
 - Investigate fuel impacts on and means of reducing the risk of plugging.
- **Exploiting Alcohols in Gasoline to Enable Lean-NO_x Reduction**
 - Investigate the potential for use of a silver-alumina catalyst using gasoline-ethanol blends as reductants; include assessment of NH₃ production for hybrid-SCR systems.
- **Biodiesel Compatibility with Emissions Control Devices**
 - Determine the Na and K poisoning mechanism for zeolite-based SCR catalysts.
- **Assess Properties, Emissions, and Compatibility of Emerging Fuels and Lubricants.**
 - Develop methodologies for sampling and analyzing lube-derived compounds in engine exhaust to aid in identifying lubricant-derived species that cause degradation of aftertreatment systems.
- **Investigate Fuel and Lubricant Formulation Impacts on GDI PM Emissions**
 - Compare morphology and reactivity of PM generated by a GDI engine using fuels with differing oxygen contents and oxygenate molecules.

Approach

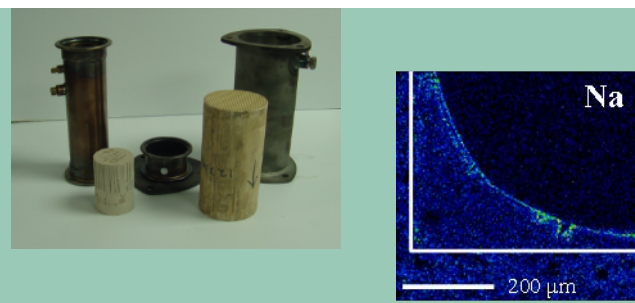
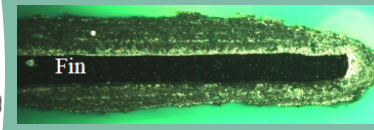
Bring together targeted, engine-based, micro-reactor, and bench reactor studies with in-depth characterization of PM, HCs, and emissions control devices to better understand fuel interactions with emissions control components.



Study fuel- and engine-specific PM to support reduced fuel penalty for emissions control.



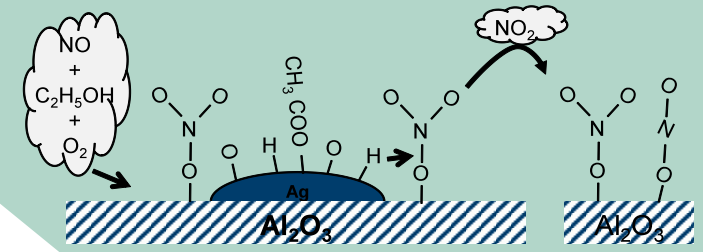
Enable examination of EGR cooler deposits to support models and component development.



Identify specific Na-related impact for each emissions control device.

New characterization techniques and engagement with industry are key enablers.

Identify mechanisms to utilize advantageous fuel characteristics.



Summary of Technical Accomplishments

Fuel Formulation Impacts on EGR System Performance

- Showed that effectiveness stabilization can exist without a removal mechanism and that plugging is a result of high HC deposition and its impact on density and thermal resistance.

Exploiting Alcohols in Gasoline to Enable Lean-NOX Reduction

- Demonstrated the possibility for significant NH_3 production and high catalyst activity over a broad temperature range for silver-alumina catalysts using ethanol reductant.

Biodiesel Compatibility with Emissions Control Devices

- Determined that more metals from biodiesel deposit in the DOC than in the SCR, but SCR degradation is more sensitive to the metals because Na and K displace ion-exchanged Cu in the zeolite structure.
- Ph.D. Granted for “The Impact of Biodiesel-based Na on the Durability of Cu-Zeolite SCR Catalysts and Other Diesel Aftertreatment Devices”

Assess Properties, Emissions, and Compatibility of Emerging Fuels and Lubricants

- Developed and used a method for sampling and analyzing phosphorus compounds in exhaust in support of studies of lubricant compatibility with aftertreatment technologies.

Investigate Fuel and Lubricant Formulation Impacts on GDI PM Emissions

- Engine and exhaust setup for experimental studies complete. Obtained particulate filter cores for reactivity studies and partnered with Umicore for application of relevant washcoats.

Does use of biodiesel blends and other non-traditional fuel formulations worsen cooler fouling compared with ULSD?

Benefit: Mitigating concerns and potential issues with EGR cooler fouling associated with expanded biodiesel use can enable broader utilization to displace petroleum consumption.

Accomplishments: Explained the conditions that cause deposits to experience either effectiveness stabilization or plugging.

- Showed that effectiveness stabilization does not imply that fouling has stopped and that stabilization does not require thermophoresis to turn off.
- Found that low-temperature conditions may cause plugging through increasing HC deposition, resulting in soot depositing into a liquid film. Fuel formulation and combustion strategy can impact this process.
- Determined that high-HC deposition increases the packing efficiency of the soot fraction, producing a higher density that persists when the HCs are removed.

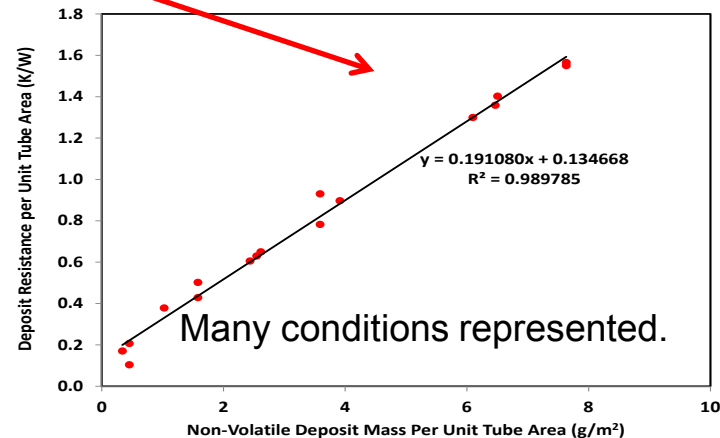
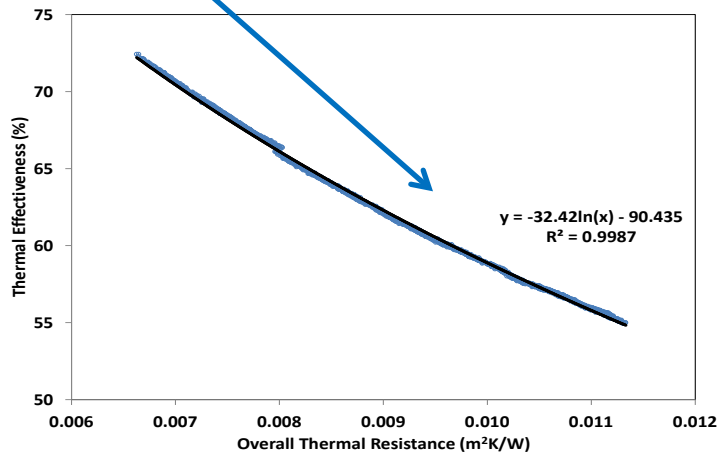
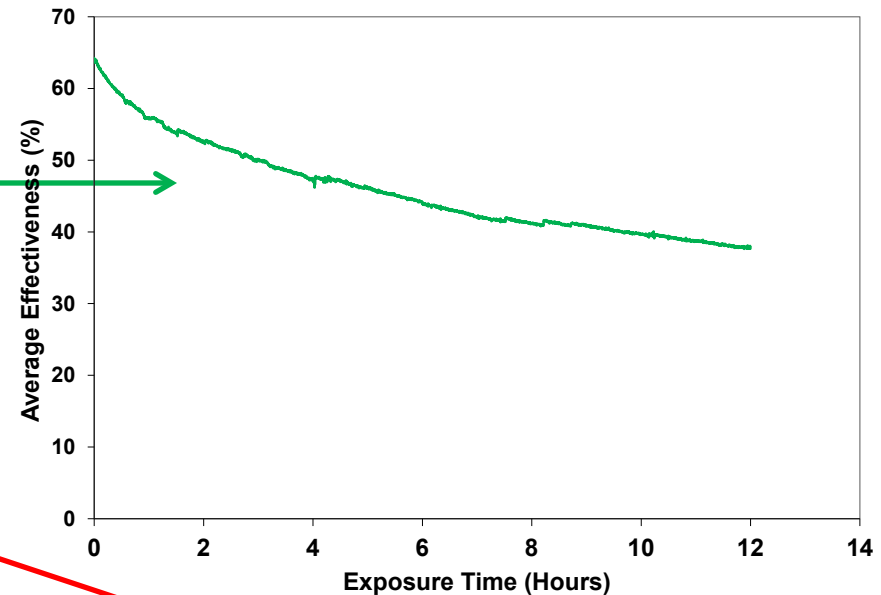
Surrogate EGR cooler tubes are employed to enable multiple analyses of deposits.

- Ford 6.4-L V-8 used as exhaust generator.
- Surrogate tubes provide more accessible samples for study than full-size coolers.
- Exhaust passed through surrogate EGR cooler tubes at constant flow rate and coolant temperature.
 - Tubes were $\frac{1}{4}$ inch square cross-section stainless steel.
 - Thermal effectiveness of tubes is assessed during exposure.
- Subsequent analyses of tube deposits:
 - Total mass of deposits
 - Volatile / non-volatile deposit mass
 - GC/MS characterization of the deposit HCs
 - Deposit layer thermal and physical properties



Why does effectiveness “stabilization” occur?

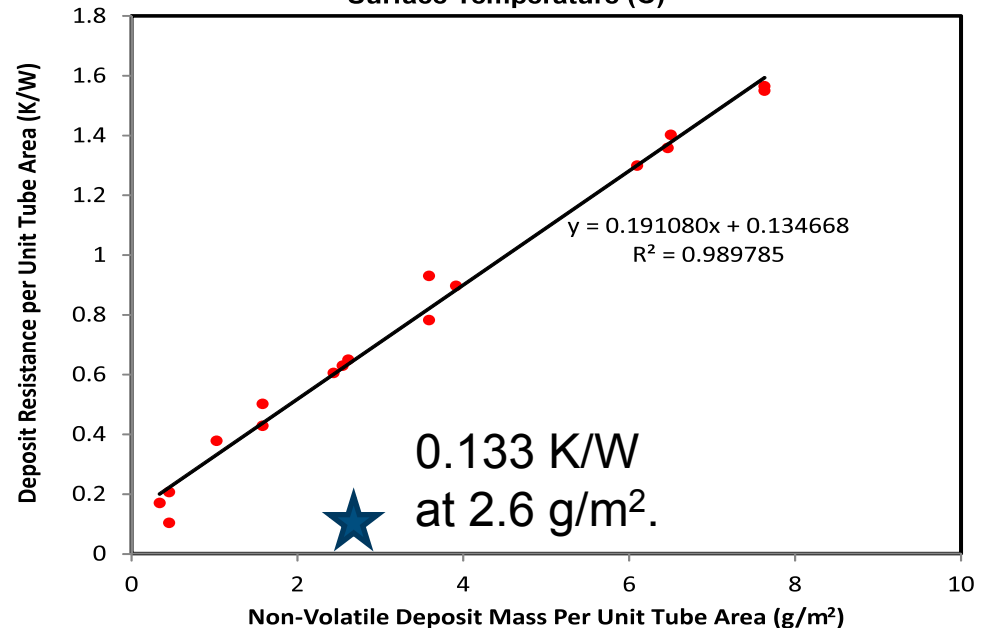
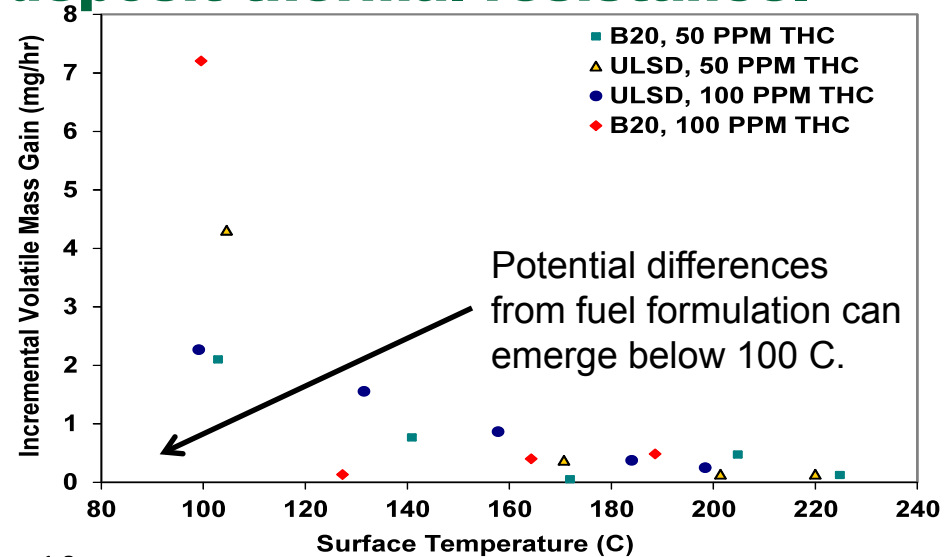
- Thermophoretic deposition does not need to stop for effectiveness to appear to approach “**stabilization.**”
 - Fouling still occurring slowly; would take ~90 hours for doubling of thermal resistance from first 12 hours.
- Thermal resistance:
 - **Linearly** related to soot mass
 - **Non-linearly** related to effectiveness



- Non-linear relationship causes effectiveness sensitivity to thermal resistance to decrease.
- No significant fuel formulation effect on “stabilization” has been identified.

Low-temperature and/or low-flow operation can lead to plugging through reduction in deposit thermal resistance.

- At low surface temperatures, HC deposition can outpace soot deposition.
- Different mechanism - Soot deposits into HC film layer.
 - Increased packing efficiency of soot, fewer and smaller void spaces in the deposit.
 - Increases soot density by ~10x. (Not just added mass of HCs.)
 - Reduces thermal deposit thermal resistance by ~5x.
- Deposit will eventually experience “stabilization,” but at ~5x thicker deposit.
 - If the gas path is too small, the thicker deposit will form a plug.



Changes in fuel formulation can increase the risk of plugging if they increase the concentration or boiling points of exhaust HC species.

- **Biodiesel blending adds high-boiling-point species to the fuel.**
 - Doesn't necessarily always increase BPs of exhaust HCs; depends on engine combustion strategy.
 - Hydrotreated oils may have less risk as they generally have lower BP HCs compared with transesterified oils.
- **Risk of plugging can be decreased by design changes such as:**
 - Use of an oxidation catalyst upstream of the cooler (EGR catalyst).
 - Use of smaller EGR cooler for low-flow conditions such as idle and cruise.
 - Increased size of gas passages.
 - Elimination of leakage or diffusive flows through the cooler.
- **Risk of plugging could be reduced by reducing the temperatures at the upper end of the diesel distillation curve.**
 - Most deposit HCs are C_{18} or higher in terms of BP.

Fuel Effects – Exploiting Alcohols in Gasoline to Enable Lean NO_x Reduction

Can broad inclusion of bio-derived alcohols in fuel improve the viability of fuel-efficient lean-burn vehicles by enabling a non-precious metal route to NO_x reduction?

Benefit: Use of lean-burn technology can reduce the tank-mileage penalty associated with high ethanol blend levels and encourage broader utilization. Taking advantage of the properties of ethanol will enable the use of non-precious metal catalyst systems for lean-NO_x reduction.

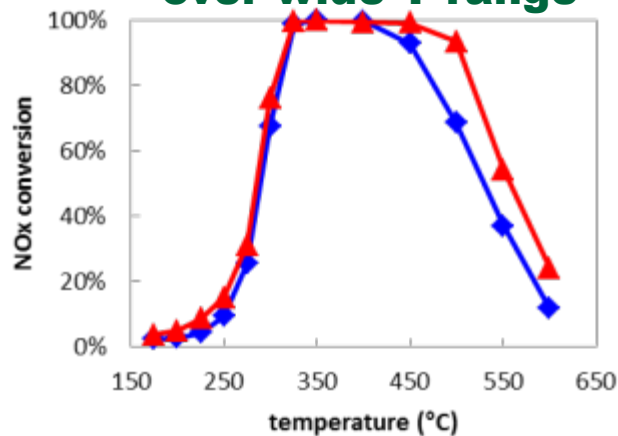
Accomplishments: Shifted focus of experiments from fundamental mechanism investigation to bench-reactor-based performance studies; showed good performance baseline using ethanol as reductant.

- Demonstrated bench-scale NH₃ production for hybrid SCR designs and investigated its dependence on C:N ratio.
- Showed good NO_x conversion over a broad temperature range with no ethanol slip above the light-off temperature.

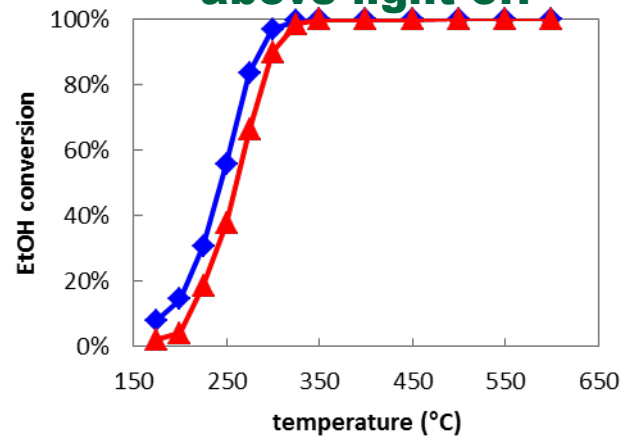
Lean NO_x control over a Ag/Al₂O₃ catalyst provides another pathway to improved efficiency with ethanol

- Ethanol's unique properties can enable increased fuel efficiency in optimized engines
- Further efficiency improvements could be realized through ethanol's efficacy in lean NO_x control over a Ag/Al₂O₃ catalyst
 - no rich or stoich excursions needed: minimal fuel penalty
 - no onboard urea or platinum group metals: low cost

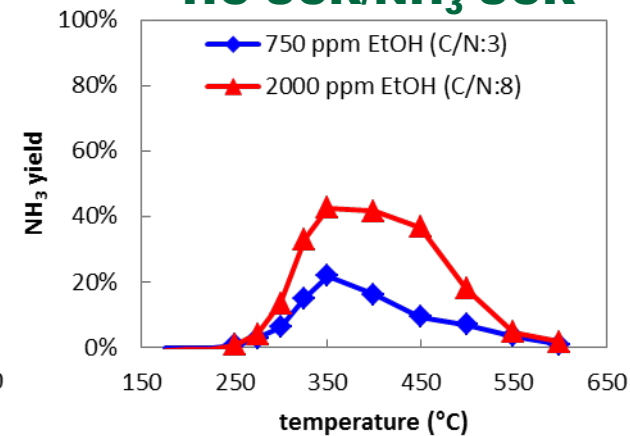
high NO_x conversion over wide T range



no HC slip above light-off



NH₃ for dual HC-SCR/NH₃-SCR



500 ppm NO, 750 or 2500 ppm ethanol, 10% O₂, 5% H₂O, balance N₂; SV 35000 hr⁻¹; 2 wt% Ag/Al₂O₃ on cordierite monolith from Catalytic Solutions

- Currently investigating effectiveness with ethanol/gasoline blends (E85, E50, E10) and butanol.
 - if other fuel components are problematic, ethanol separation may be an option.

Fuel Effects – Biodiesel-compatibility with emissions control devices

Are metal specifications ($\text{Na}+\text{K} < 5 \text{ ppm}$, $\text{Ca}+\text{Mg} < 5 \text{ ppm}$) for biodiesel sufficient for B20 compatibility with emissions control devices at end of life?

Benefit: Understanding the potential impact of fuel-borne metals will help OEMs make informed decisions when considering the adoption of B20 certification.

Accomplishments: Determined that more metals from biodiesel deposit in the DOC than in the SCR, but SCR degradation is more sensitive to the metals because Na and K displace ion-exchanged Cu in the zeolite structure.

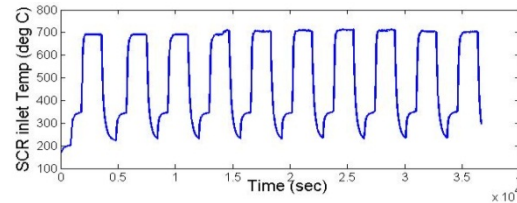
- Ca poisoning is much less severe than Na or K poisoning.
- Collaboration team awarded Biodiesel Researchers of the Year Award for 2012.

Biodiesel compatibility with modern emissions control devices: impact of fuel-borne metals Na, K, and Ca

- Collaboration with NREL, NBB, MECA, and Ford focusing on light duty applications
 - full production exhaust systems from 2011 Ford F250; DOC→SCR→DPF



Thermal cycling

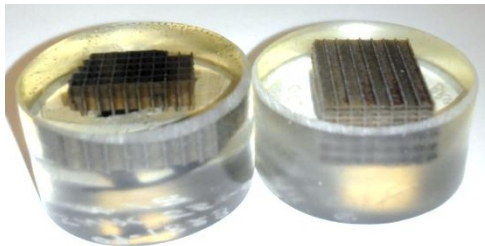


FTP data evaluated



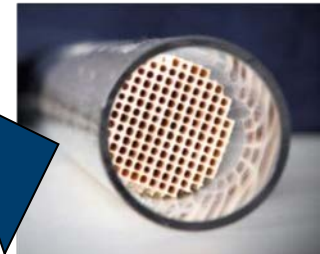
NREL leading engine operation

- Na, K, and Ca plus thermal exposure; ULSD-only too
- Coordinating with MECA+NBB



Ford leading catalyst functionality study

- Sectioned study of DOC and SCR
- Determine what level of Na, Ca, and K leads to decrease in performance

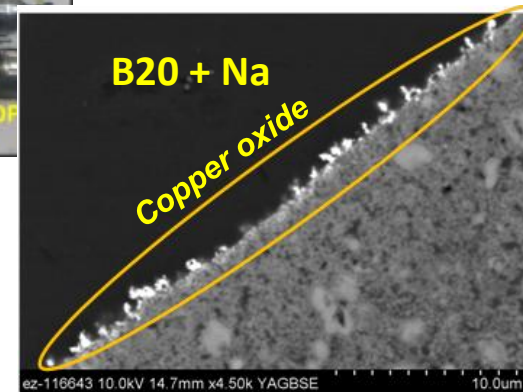


Section & evaluate



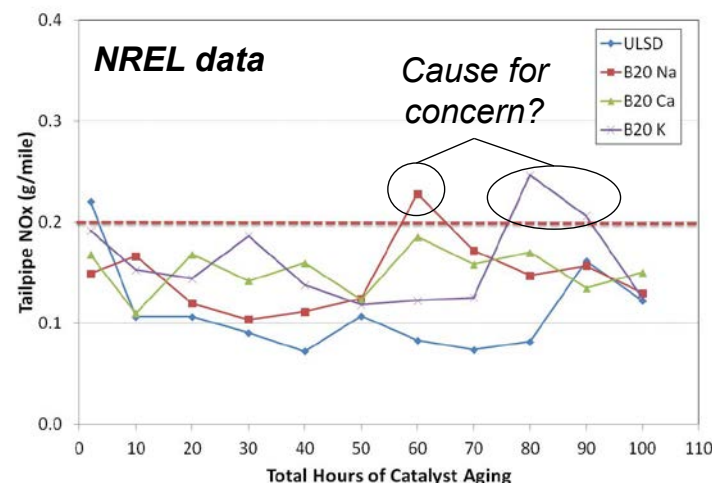
ORNL leading materials characterization

- Identify level of Na, Ca, and K in each section of the emissions control devices
- DPF materials characterization
 - Co-funded by Propulsion Materials

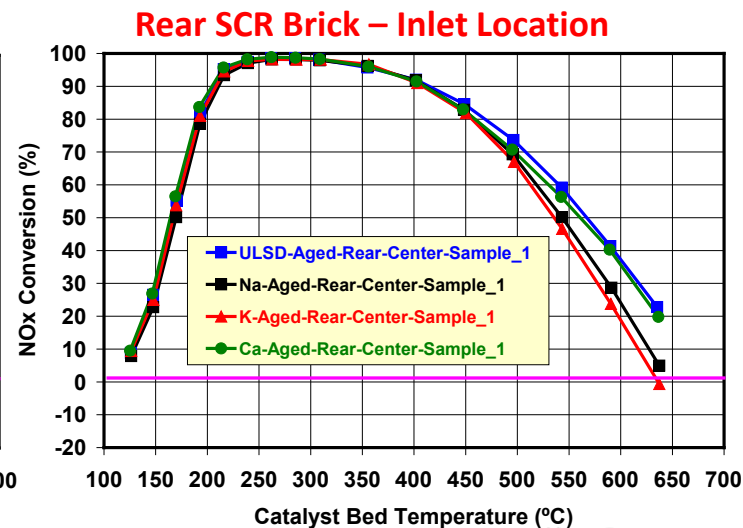
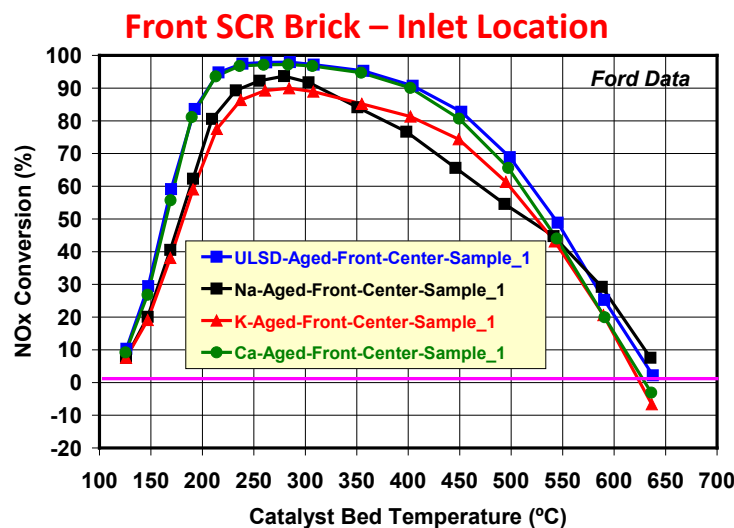


Fully aged system meets emissions regulations; however, Na and K show an impact on SCR.

- NREL performed engine-based vehicle exposure and vehicle FTP evaluation
- Vehicle met final emissions target...however:
 - K and Na exposures showed points above NO_x std
 - Average NO_x is higher for each metal-aged system
- Parts removed and cut into sections for:
 - individual evaluation (Ford)
 - materials characterization (ORNL)
- DOC evaluation only showed minor deactivation w/ metals
 - CO and HC standards easily met in FTP

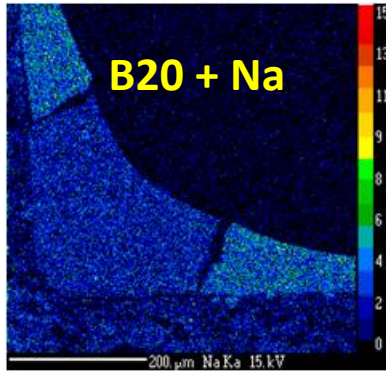


- SCR evaluation shows inlet of front brick is significantly deactivated with Na and K
 - not Ca
- Rear brick is not significantly affected

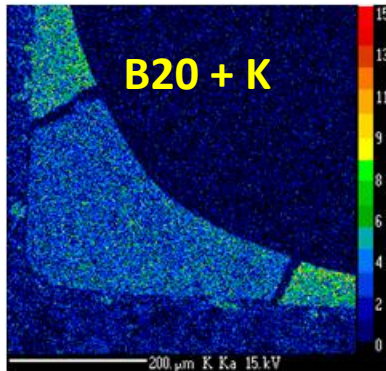


ORNL identifies nature and location of Na and K deactivation in Cu-zeolite SCR.

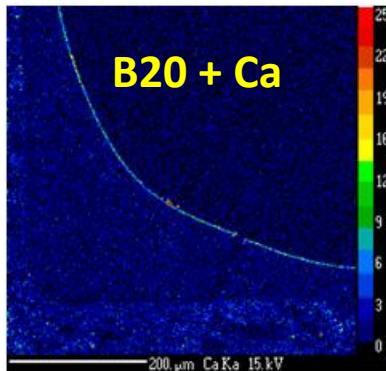
Na - EPMA



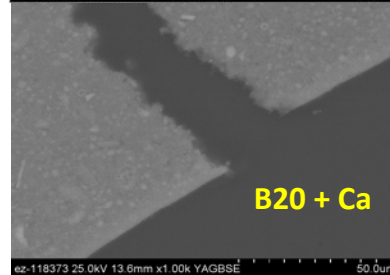
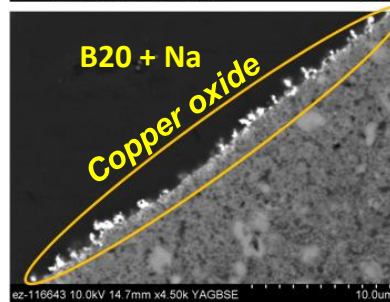
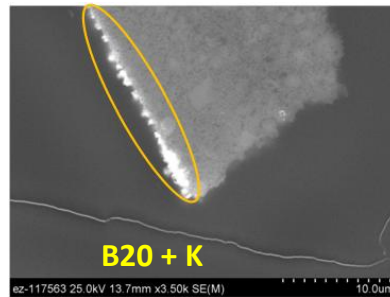
K - EPMA



Ca - EPMA



Element	wt%
C	32.09
O	17.49
Al	1.11
Si	13.71
Cu	33.14



- Na and K penetrate throughout SCR washcoat
 - In areas of high Na and K → Cu decreases
- With Na and K samples, CuO layer shown on the surface
 - Indicative Na/K substitution for Cu in zeolite
- Discoloration on cores shown to be CuO and penetrates ~1/3 into front brick;
 - ~20% of total SCR volume
- Conclusion: while FTP emissions met at 150,000 mile exposure, failed emission standard could occur with:
 - more stringent emissions or
 - out of specification fuel

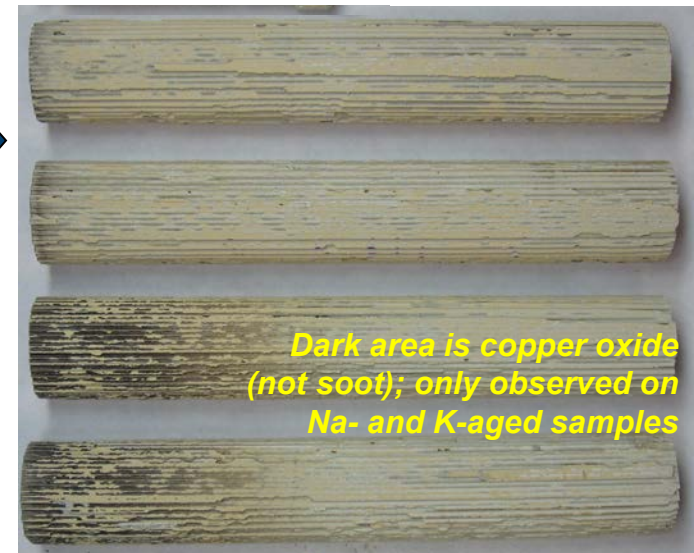
ULSD-Front

flow

Ca-Front

Na-Front

K-Front



Collaborators and Partners

- **Fuel Effects on EGR Cooler Fouling**
 - Ford/GM/Modine: experimental guidance
 - Ford and Navistar making use of our work
 - ORNL Advanced Manufacturing Center (DOE-AMO)
 - ORNL Neutron Sciences (Neutron Imaging)
- **Exploiting Alcohols in Gasoline to Enable Lean-NO_x Reduction:**
 - Galen Fisher, Univ. Michigan (technical advisor)
 - Catalytic Solutions (catalysts)
- **Biodiesel-based Na Impacts on Emissions Control Devices:**
 - NREL/Ford/MECA/National Biodiesel Board: Biodiesel-aged collaborative effort
 - University of Tennessee, Chalmers University: graduate research
 - CLEERS: evaluation protocols
- **Investigate Fuel and Lubricant Formulation Impacts on GDI PM Emissions:**
 - Umicore (gasoline particulate filter washcoating)

Future Directions

- **Fuel Effects on EGR Cooler Fouling:**
 - Concluding this year; funding shifting to other research thrust areas within fuels and lubricants program.
- **Exploiting Alcohols in Gasoline to Enable Lean-NO_x Reduction:**
 - Continue performance investigation with ethanol-gasoline and butanol-gasoline blends.
- **Biodiesel-based Na Impacts on Emissions Control Devices:**
 - Continue with examination of scope of heavy duty concern.
 - Examine advanced lubricant-based impacts on emissions controls.
- **Assessment of Properties, Emissions, and Compatibility of Emerging Fuels:**
 - Conduct studies to determine key pathways and potential mitigation strategies for phosphorus degradation of aftertreatment devices.
- **Investigate Fuel and Lubricant Formulation Impacts on GDI PM Emissions:**
 - Carry out studies of GDI-generated soot using gasoline as well as ethanol and butanol blends to aid in identifying fuel and lubricant impacts on PM formation and reduction pathways.

As always, we welcome specific concerns from industry, whether in these areas or other topics, for future studies.

Summary

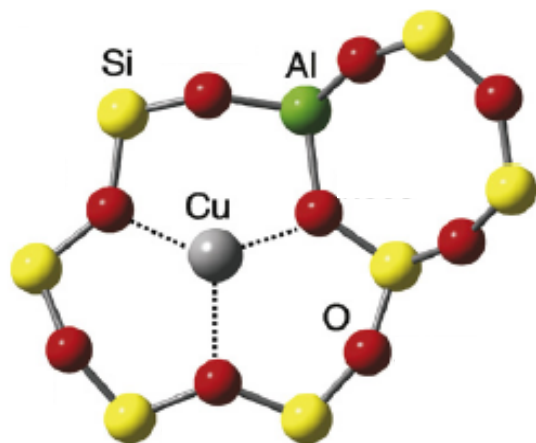
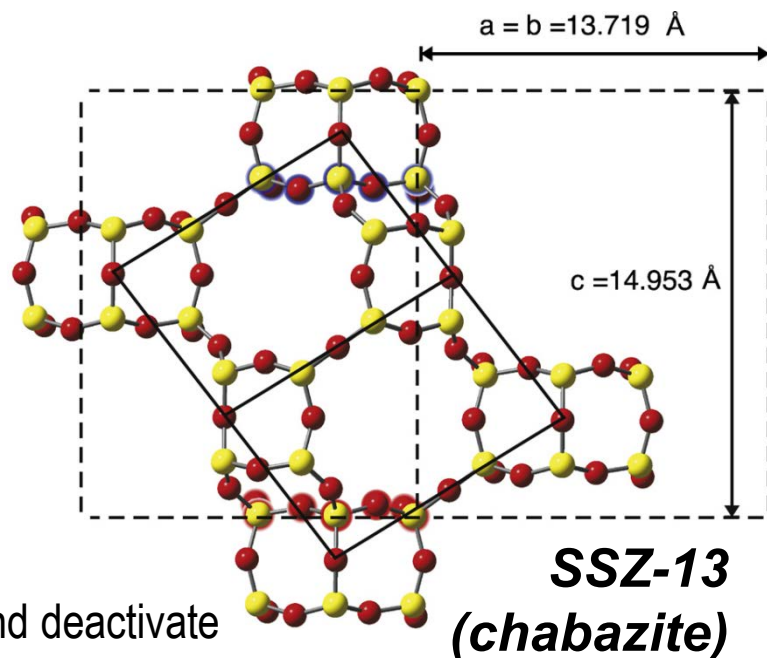
- **Relevance**: These studies are targeted towards providing data and predictive tools to address gaps in information needed to enable increased use of biofuels. (DOE Technical Barrier)
- **Approach**: The approach being pursued is to bring together targeted, engine-based studies using biofuels with in-depth characterization of PM and HCs to better understand behavior for specific technologies. (Currently emissions control devices and EGR Systems)
- **Collaborations**: Collaborations with several industry stakeholders and universities are being used to maximize the impact of this work.
- **Technical Accomplishments**:
 - Explained conditions that lead to EGR cooler effectiveness stabilization or plugging and how fuel formulation changes can impact the process.
 - Showed that silver-alumina catalysts have the potential for NH_3 production for hybrid-SCR systems and that NO_x conversion is high and ethanol slip low over a broad temperature window.
 - Explained why Na and K poison zeolite-based SCR systems and uncovered potential concern in heavy-duty applications.
- **Future Work**: Plans are in place; industry input towards those plans or other fuel-emissions control effect concerns is needed and welcomed.

TECHNICAL BACKUP SLIDES

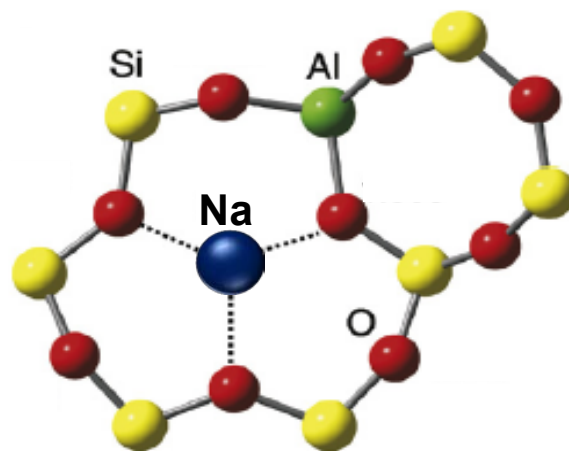
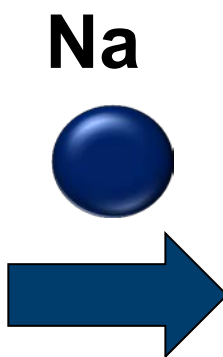
NPBF Effects – Biodiesel-compatibility with emissions control devices

Anatomy of Cu-zeolite

- Initial zeolite contains Si, Al, O and H
 - unexchanged zeolites w/ H-atoms on surface
- To catalytically activate zeolite, metals are “exchanged” with adsorbed H-atoms
 - atomically dispersed; aqueous addition
 - directly bonds to zeolite structure
- Over exchange, results in Cu-oxide formation
- Other metals, e.g. Na and K, can displace the metal and deactivate the catalyst.

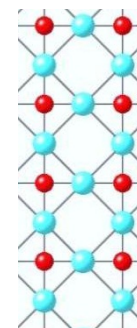


Active SCR Catalyst



Deactivated SCR Catalyst

Cu_xO



Images adapted from McEwen et al. *Catalysis Today* 184 (2012) 129.

Lubricant Additive Effects on Aftertreatment: Measurement & Speciation of Phosphorus in Exhaust

Issues:

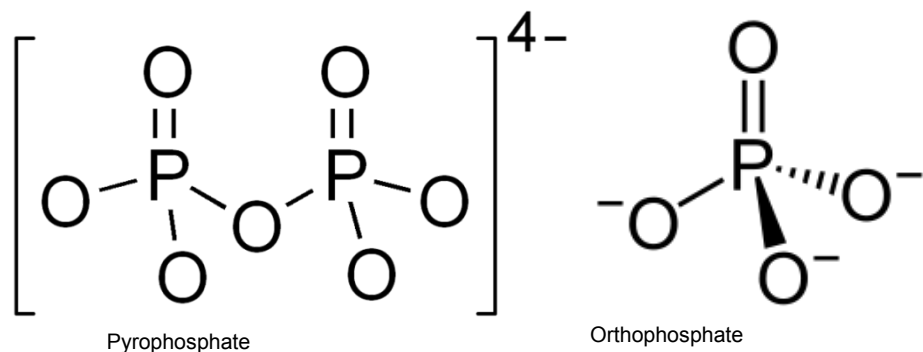
- Phosphorus can significantly alter catalyst performance and aging characteristics.
- Different forms of phosphate may interact differently with the substrate and/or washcoat of the catalyst, and little is known about which form(s) are the most important participants.

Approach:

Collect gas and particle phase samples during engine operations followed by novel extraction, concentration, and analysis. (Example at right.)

Benefit:

Allows examination of the impact of different forms of phosphate on emissions control devices to aid in formulation of high-efficiency lubricants.



Above example shows two of the forms phosphorus can take in engine exhaust.

Analysis Example:

Ammonium Phospho-Molybdate Complex

This method indicates orthophosphate in concentrated condensate samples colorimetrically.



Investigate Fuel and Lubricant Formulation Impacts on GDI PM Emissions: Initial Fuel Oxygen Impact Study

- Specific focus on fuel oxygen effect on PM characteristics
 - Ethanol, butanol blends at constant fuel oxygen content levels
- Mimicking throttle “tip-in” point for acceleration
 - Rich operation ($\lambda = 0.91$) , medium high load
 - Using a modified GM 2.0 L (L850) engine with full-pass control
- Collect samples to examine changes in PM size and morphology:
 - EEPS and transmission electron microscopy to examine changes in primary particle size with fuel/air mixing and flame temperature.
- Assess changes in PM chemistry:
 - Filter collection and Pyrolysis GC-MS analysis
- Determine Soot Oxidation Kinetics:
 - GPF cores coated by Umicore
 - Bench flow reactor studies with cores

Status: Engine and exhaust system set-up complete. GPFs acquired and washcoated. Experimental campaign planned in April-May of 2013.



Exhaust system and engine
Inset: Sample holder for exposure of four 1” GPFs